

PATENT

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of : Hsu et al.  
Serial No. : Unknown (Division of USSN 09/232,989)  
Filing Date : Herewith  
For : AROMATIC POLYOL END-CAPPED UNSATURATED  
POLYETHERESTER RESINS AND RESIN COMPOSITIONS  
CONTAINING THE SAME HAVING IMPROVED CHEMICAL  
AND/OR WATER RESISTANCE  
Attorney Docket No. : CCP-3342-B

**CERTIFICATION UNDER 37 CFR 1.8(a) and 1.10**

I hereby certify that, on the date shown below, this correspondence is being:

**Mailing**

☒ deposited with the United States Postal Service in an envelope addressed to the Assistant Commissioner for Patents,  
Washington, D.C. 20231  
**37 CFR 1.8(a)** **37 CFR 1.10**  
☐ with sufficient postage as first class mail ☒ As "Express Mail Post Office to Addressee" Mailing Label No. EL609566205US

**Transmission**

☐ transmitted by facsimile to Fax No \_\_\_\_\_ addressed to Examiner \_\_\_\_\_ at the Patent and Trademark Office.

Date: March 28, 2001

Jul R. Paul

BOX PATENT APPLICATION  
Assistant Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Sir:

This application is a division of U.S. Serial No. 09/232,989. Prior to substantive examination, Applicant requests the following amendments be made in the application.

**IN THE CLAIMS**

Please amend the claims as shown in the attached replacement sheets submitted under 37 C.F.R. § 1.12(c). Please cancel Claims 1-38 without prejudice, and add new Claims 39-82, as provided on the enclosed replacement sheets.

**IN THE SPECIFICATION**

Please amend the specification at page 1, by inserting after the title:

**--CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a division of U.S. Pat. Application Serial No. 09/232,989, filed January 19, 1999, now U.S. Patent No. 6,211,305, issued April 3, 2001, which claims the benefit of U.S. Provisional Application No. 60/071,951, filed January 20, 1998--

**REMARKS**

The present application is a division of USSN 09/232,989, to issue as U.S. Pat. No. 6,211,305 on April 3, 2001.

Consideration of the newly added claims is requested. Claims 39-82 have been added and are presently pending. Claims 1-38 have been canceled without prejudice. Support for the claims is in the original claims as filed.

The claims are drawn to curable thermoset resin compositions, laminates, and methods of reducing blistering of a gel-coated fiber-reinforced polymer. The claims presented herein were the subject of a restriction in the parent application S/N 09/232,989, and are being pursued for prosecution in the presently filed application.

It is respectfully submitted that the claims are in condition for allowance and notification to that effect is earnestly solicited. The Examiner is urged to telephone the undersigned attorney if any questions should arise.

Respectfully submitted,

*Kristine M. Strodthoff*

Kristine M. Strodthoff  
Registration No. 34,259

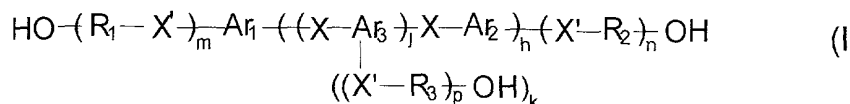
Dated: March 28, 2001

P.O. ADDRESS:

WHYTE HIRSCHBOECK DUDEK S.C.  
111 East Wisconsin Avenue, Suite 2100  
Milwaukee, Wisconsin 53202  
(414) 273-2100

38. A curable thermoset resin composition, comprising:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol comprising at least one non-primary hydroxy group, the aromatic polyol represented by the formula



wherein Ar<sub>1</sub>, Ar<sub>2</sub> and Ar<sub>3</sub> each independently represents an aromatic group; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent heteroatom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

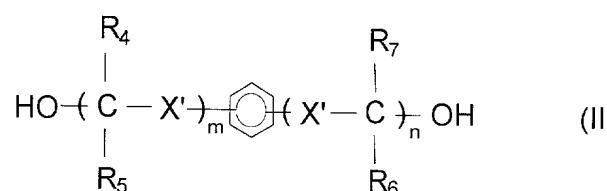
(D) at least one curing agent.

39. The composition according to Claim 38, wherein, in the aromatic polyol, Ar<sub>1</sub>, and Ar<sub>2</sub> and Ar<sub>3</sub> when present, each represent a phenylene ring.

40. The composition according to Claim 38, wherein, in the aromatic polyol, each X, when present, represents a hydrocarbylene or hydrocarbylidene group and each X' represents a hetero atom.

41. The composition according to Claim 38, wherein, in the aromatic polyol, h is 0.

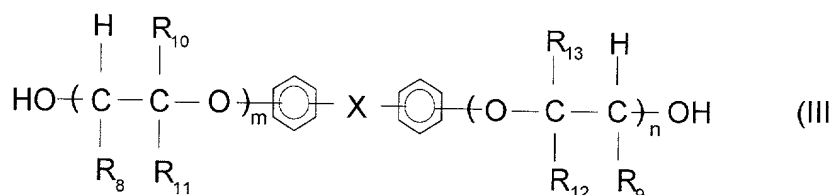
42. The composition according to Claim 41, wherein the aromatic polyol comprises at least one primary hydroxy group and is represented by the formula:



wherein R<sub>4</sub> to R<sub>7</sub> each independently represent a hydrogen atom or a hydrocarbyl group, provided that at least one hydroxy group is a nonprimary hydroxy group.

43. The composition according to Claim 38, wherein, in the aromatic polyol, h is 1.

44. The composition according to Claim 43, wherein the aromatic polyol comprises at least one primary hydroxy group and is represented by the formula:



wherein each of  $R_8$  to  $R_{13}$  represent a hydrogen atom or a predominantly hydrocarbyl group, provided that at least one of  $R_8$  and  $R_9$  is not an hydrogen atom, X represents  $-(CH_3)_2-$ ,  $-S-$  or  $-O-$ , and m and n represent integers which individually are in the range from 1 to 5.

45. The composition according to Claim 44, wherein the aromatic polyol is a propylene oxide adduct of bisphenol A.

46. The composition according to Claim 38, wherein, in the aromatic polyol, h is 1 and j is in the range from 1 to 5.

47. The composition according to Claim 46, wherein X is a methylene, alkylene or alkylidene group.

48. The composition according to Claim 46, wherein the aromatic polyol is an alkoxyated novolac-type polymer.

49. The composition according to Claim 46, wherein the aromatic polyol is a propoxylated novolac-type polymer.

50. The composition according to Claim 38, wherein the at least one unsaturated polyetherester resin comprises the reaction product of at least one polyether and at least one ethylenically unsaturated anhydride or dicarboxylic acid wherein the anhydride or dicarboxylic acid are inserted into carbon-oxygen bonds of the polyether.

51. The composition according to Claim 50, wherein the polyether is a polyether glycol having an average hydroxyl functionality of about 2 to about 6, a hydroxyl number of about 28 to about 260 mg KOH/g, and a number average molecular weight of about 400 to about 12,000.

52. The composition according to Claim 38, wherein the unsaturated polyester resin (B) is derived from at least dicyclopentadiene, an unsaturated carboxylic anhydride, and a glycol.
53. The composition according to Claim 38, wherein the vinyl monomer (C) comprises styrene.
54. The composition according to Claims 38, wherein the curing agent (D) comprises a catalyst system comprising a free radical initiator and an accelerator.
55. The composition according to Claim 38, further comprising at least one aromatic vinyl ester resin.
56. The composition according to Claim 55, wherein the at least one aromatic vinyl ester comprises a reaction product of epichlorohydrin and bisphenol A, which is further reacted with a vinyl acid.
57. The composition according to Claim 55, wherein the at least one aromatic vinyl ester comprises the reaction product of epichlorohydrin with a novolac-type resin, which is further reacted with a vinyl acid.
58. The composition according to Claim 38, further comprising a second unsaturated polyetherester resin other than the unsaturated polyetherester resin (A).
59. The composition according to Claim 58, wherein the second unsaturated polyetherester resin comprises an unsaturated polyesterester resin end-capped with at least one end-capping compound selected from the group consisting of dicyclopentadiene, an epoxy-containing compound, and combinations thereof.

60. An intermediate in the form of a sheet for making a skin laminate, the intermediate comprising reinforcing fibers and the curable thermoset resin composition of Claim 38.

61. A gel coated polymer laminate comprising at least one fiber-reinforced polymer layer, at least one gel coat layer, and at least one thermoset resin layer interposed between the at least one fiber-reinforced polymer layer and the at least one gel coat layer, wherein the at least one thermoset resin layer comprises the skin laminate intermediate of Claim 60, wherein the curable thermoset resin composition is cured.

62. The gel coated laminate of Claim 61, wherein the fiber-reinforced polymer layer comprises a reinforcing fiber and a polyester resin.

63. The gel coated laminate of Claim 61, wherein the ratio of the average thickness of the at least one fiber-reinforced polymer layer and the average thickness of the at least one thermoset resin layer is about 6:1 to about 2:1.

64. A fiber-reinforced polymer composite comprising a cured composition comprising the curable thermoset resin composition of Claim 38, and a reinforcing fiber.

65. A gel coated fiber-reinforced polymer comprising the fiber-reinforced polymer composite of Claim 64 and a gel coat.

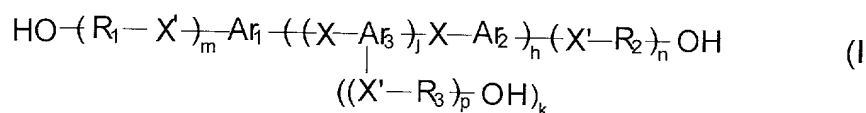
66. A gel coated polymer laminate comprising at least one fiber-reinforced polymer layer, at least one gel coat layer, and at least one thermoset resin layer interposed between the at least one fiber-reinforced polymer layer and the at least one gel coat layer, wherein the at least one thermoset resin layer comprises the curable thermoset resin composition of Claim 38.

67. The gel coated polymer laminate of Claim 66, wherein the fiber-reinforced polymer layer comprises a reinforcing fiber and a polyester resin.

68. The gel coated polymer laminate of Claim 66, wherein the ratio of the average thickness of the at least one fiber-reinforced polymer layer and the average thickness of the at least one thermoset resin layer is about 6:1 to about 2:1.

69. A curable thermoset resin composition, comprising:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol and the reaction product of at least one acid-terminated unsaturated polyetherester resin and at least one aromatic polyol having at least one non-primary hydroxy group; the at least one aromatic polyol represented by the formula:



wherein Ar<sub>1</sub>, Ar<sub>2</sub> and Ar<sub>3</sub> each independently represents an aromatic group; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent hetero atom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

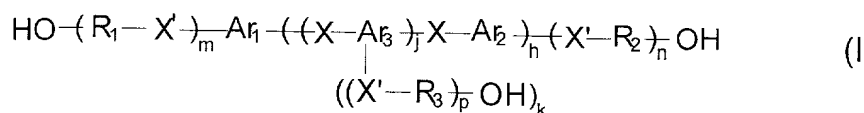
(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

(D) at least one curing agent.



70. A method for making a curable thermoset resin composition, comprising combining:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol, the aromatic polyol comprising at least one non-primary hydroxy group and represented by the formula:



wherein Ar<sub>1</sub>, Ar<sub>2</sub> and Ar<sub>3</sub> each independently represents an aromatic group; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent heteroatom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

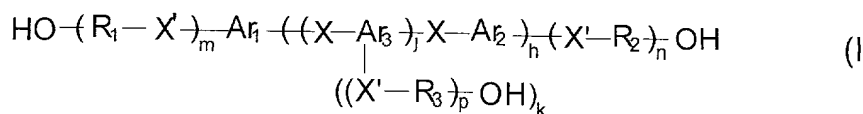
(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

(D) at least one curing agent.

71. An intermediate for making a curable thermoset resin composition comprising

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol, the aromatic polyol comprising at least one non-primary hydroxy group and represented by the formula:



wherein Ar<sub>1</sub>, Ar<sub>2</sub> and Ar<sub>3</sub> each independently represents an aromatic group; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represents a non-aromatic predominantly hydrocarbyl group; each X and X' independently represents a hydrocarbylene group, a hydrocarbylidene group, a divalent heteroatom or group, an ester linkage, or a combination thereof; each X' can also represent a covalent bond; h and k each independently represent an integer equal to 0 or 1; j represents an integer in the range from 0 to 5; and m, n, and p each independently represent an integer in the range from 1 to 5, provided that at least one hydroxy group of formula (I) is a nonprimary hydroxy group;

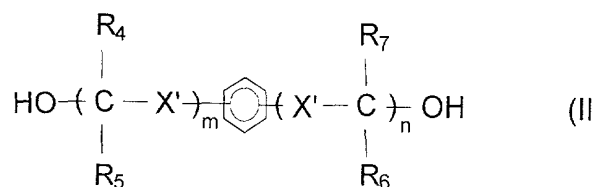
(B) at least one unsaturated polyester resin having a weight ratio of the number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10; and

(C) about 20 to about 50 wt.% of at least one vinyl monomer.

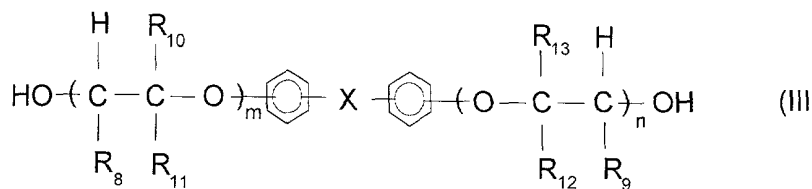
72. The intermediate according to Claim 71, further comprising a second unsaturated polyetherester resin other than the unsaturated polyetherester resin (A).

73. A curable thermoset resin composition, comprising:

(A) at least 5 wt.% of at least one unsaturated polyetherester resin at least partially end-capped with an aromatic polyol comprising at least one primary hydroxy group, the aromatic polyol represented by the formula:



wherein R<sub>4</sub> to R<sub>7</sub> each independently represent a hydrogen atom or a hydrocarbyl group, provided that at least one hydroxy group is a nonprimary hydroxy group, or



wherein each of R<sub>8</sub> to R<sub>13</sub> represent a hydrogen atom or a predominantly hydrocarbyl group, provided that at least one of R<sub>8</sub> and R<sub>9</sub> is not an hydrogen atom, X represents -C(CH<sub>3</sub>)<sub>2</sub>-, -S- or -O-, and m and n represent integers which individually are in the range from 1 to 5, or comprises an aromatic polyol prepared by alkoxyating a novolac-type polymer;

(B) at least one unsaturated polyester resin having a number average molecular weight to the average number of double bonds per polymer molecule in the range from about 200 to about 400, in an amount such that the weight ratio of polyester resin (B) to polyetherester resin (A) is in the range from about 10:90 to about 90:10;

(C) about 10 to about 70 wt.% of at least one vinyl monomer; and

(D) at least one curing agent.

74. The composition according to Claim 73, wherein the unsaturated polyester resin (B) is derived from at least dicyclopentadiene, an unsaturated carboxylic anhydride, and a glycol; the at least one vinyl monomer (C) comprises styrene; and the at least one curing agent (D) comprises a catalyst system comprising a free radical initiator and an accelerator.

75. The composition according to Claim 73, further comprising at least one aromatic vinyl ester resin.

76. An intermediate in the form of a sheet for making a skin laminate comprising reinforcing fibers and the curable thermoset resin composition according to Claim 73.

77. A fiber-reinforced polymer composite comprising a cured composition comprising the curable thermoset resin composition of Claim 73 with a reinforcing fiber.

78. A gel coated fiber-reinforced polymer comprising the fiber-reinforced polymer composite of Claim 77 and a gel coat.

79. A method for reducing blistering of a gel coated fiber-reinforced polymer comprising:  
applying a curable gel coat composition to a mold;  
at least partially curing the gel coat composition;  
applying at least one layer of at least one curable thermoset resin composition according to Claim 38 to the at least partially cured gel coat composition;  
at least partially curing the curable thermoset resin composition;  
applying at least one fiber-reinforced polymer layer to the at least partially cured thermoset resin composition layer; and  
curing the thermoset resin composition layer to form the gel coated fiber-reinforced polymer.

80. An article produced by the method of Claim 79.

81. A method for reducing blistering of a gel coated fiber-reinforced polymer comprising:  
applying a curable gel coat composition to a mold;  
at least partially curing the gel coat composition;

applying at least one layer of the skin laminate intermediate of Claim 60 to the at least partially cured gel coat composition;

at least partially curing the curable thermoset resin composition; and

applying at least one fiber-reinforced polymer layer to the at least partially cured thermoset resin composition layer; and

curing the thermoset resin composition layer to form the gel coated fiber-reinforced polymer.

82. An article produced by the method of Claim 81.